A Polarographic Study of the Corrosion of Iron and Some Ferrous Alloys by Sulfur Dioxide

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CHAPTER I

INTRODUCTION

General Theories of Corrosion

The problem of corrosion of metals has long been of economic significance, and a great amount of work has been done in the field. It has been estimated that as much as two per cent of the total tonnage of metal in use must be replaced annually due to corrosion, and that a large and increasing proportion of the annual production will be required to replace that rendered unserviceable by corrosion. It has also been estimated that the annual loss to the United States through the corrosion of metals is approximately five to five and one-half billion dollars.[1] Thus research toward a better understanding of corrosion processes and mechanisms is of great importance.

Corrosion is defined as the destruction of a metal by some chemical or electrochemical action of the environment, and is distinguished from erosion, which is the mechanical destruction of a metal by abrasion. The two often combine, however, to give an accelerated action to the destruction of a metal. For the purposes of this discussion only corrosion will be considered.

A survey of the literature indicates that there are at least six theories which have been advanced to explain the corrosion mechanism. These are particularly well summarized by Speller.[2] Several of these have been proved to be in error, and others have been discarded for want of sufficient evidence. The role of oxygen has been well studied and is probably the best understood of any substance which may cause corrosion.

At present, perhaps the most widely accepted theory of the corrosion mechanism in solutions is that of the electrochemical cell. Whitney,[3] in 1903, advanced the idea of a cell in which iron was the one electrode and hydrogen the other. This theory has been expanded with regard to solutions. A survey of the literature indicates that it is now the only generally accepted idea.

According to this theory, since each metal has a tendency to form ions in solution, commonly called the electrode potential, ions are formed at some point on the surface of the metal and the metal goes into solution. In order to maintain electrochemical neutrality some ion already in solution must be plated out. In the simplest case, that of an acid solution, hydrogen is evolved. In effect, a small galvanic cell is established, the anode being at that point at which the metal goes into solution, and the cathode that point at which a corresponding reduction takes place. In the simplest cases, hydrogen may be evolved as gaseous molecular hydrogen, or the atomic hydrogen may be combined with oxygen to give water. The basic reactions for such cases with a divalent metal present are as follows:

1. $M \rightarrow M^{++} + 2\,e$
2. $2\,H_2O + 2\,e \rightarrow 2\,OH^- + 2\,H$
3. $2\,H \rightarrow H_2$
4. $2\,H + 1/2\,O_2 \rightarrow 2\,H_2O$

The overall reaction for an acid solution may thus be summarized:

$$M + 2H^{+} \rightarrow M^{++} + H_2$$

The corresponding reaction in neutral or alkaline solution in which oxygen is present is:

$$M + 1/2\ O_2 + H_2O \rightarrow M^{++} + 2\ OH^{-}$$

The role of oxygen is thus that of a cathodic depolariser. It removes the film of hydrogen formed at the cathode, thus allowing the reaction to continue, and also reduces any counter electromotive force which may be built up by products of the corrosion reaction.

Support to the idea that oxygen acts as a cathodic depolariser is given by the work of Evans.[4] He was able to show that the center of a drop of electrolyte on a metallic surface automatically became the anode of a galvanic cell, and the edge at which oxygen was readily available became the cathode. In situations wherein oxygen was readily accessible throughout the area, other factors determined the anodic and cathodic areas.

The role played in the corrosion mechanism by compounds known to accelerate the destruction of a metal, particularly iron or steel, is not completely clear. Evans[5] states that in the presence of oxidising acids the cathodic reaction of the galvanic cell consists of the reduction of the oxidising agent, and that in such cases there is no reason to believe that there are distinct anodic and cathodic areas. He assumes that the anodic and cathodic portions of the cell proceed alternately at the same point, or concurrently at points exceedingly close together.

In the case where two different metals are present in a conducting solution, it has been well established that the mechanism is that of a galvanic cell, the anode and the cathode being determined by the relative positions of the metals in the electroactive series as well as by the environment.[6,7] This same action may be responsible for attack under conditions in which the surface of the metal is not homogeneous, as for example, the presence of mill scale on polished iron surfaces. Mears and Brown[8] have investigated many other factors which may be responsible for the setting up of potential differences between different parts of a metal surface.

Attempts have been made to classify some forms of corrosion in solution as "direct chemical attack." This must be regarded as arbitrary in nature in that while a gain and loss of electrons is postulated, the term "electrochemical" is used only if the anodic and cathodic areas can be separated. The mechanism is essentially the same for either case. Perhaps the best summary is that given by Speller:[9]

> The number of factors involved and their effect on each other is sometimes bewildering. When water is present, the primary reactions are electrochemical . . . but no matter how the reader may interpret the effect of the many influences bearing on these phenomena, most of the underlying fundamental reactions, without which corrosion cannot occur, are now recognized as electrochemical . . .

The electrochemical attack may be stifled when the solution is capable of yielding a sparingly soluble substance as a direct anodic product. The formation of a similiar cathodic product may also slow down corrosion by preventing the release of hydrogen or the substance normally appearing at the cathode. Either type of action is known as inhibition and agents which provide this action are constantly sought. Many are well known and are commonly used.

Another mechanism by which corrosion may be prevented or greatly slowed down is that of passivation. Passivation is best generally defined by Uhlig and Mears:[10]

> A metal or alloy is passive when it substantially resists corrosion in an environment where thermodynamically there is a large free energy decrease associated with its passage from the metallic state to appropriate corrosion products.

A familiar case of such action is iron in concentrated nitric acid solutions. The difference between passivation and inhibition may best be understood by considering that passivation deals with changes in or on the metal surface itself, while inhibition deals with changes in the corrosion process by the environment. A metal may conceivably be passivated by treatment in one environment and used with some freedom from corrosion in another, whereas the inhibitor must be within the environment in which the metal is to be used and such treatment will not aid in freedom from corrosion in any other environment. Uhlig and Mears,[10] Evans,[11] and Eldredge and Warner[12] give excellent discussions of these subjects.

Essentially the method by which corrosion is prevented in either case is some type of film formation. Evans[11] states: ". . .most cases of passivity . . . appear to be attributable, directly or indirectly to a protective film, although not always an oxide film." Glasstone[13] also holds this view.

In the absence of solutions it has been noted that many agents attack metals with resultant corrosion. These effects have been particularly studied at elevated temperatures. This action is also loosely classified as direct chemical action. Riley[14] states:

> The presence of sulfur-containing gases and moisture appreciably increases the oxidation rate of copper, iron, and many other metals and alloys in air . . . The mechanism of the behaviour of these constituents is not well known.

Methods of Corrosion Testing

Corrosion tests may be divided into two types, those which duplicate full service conditions, and those which may be performed under special conditions either in the laboratory or under other non-service conditions.

From the standpoint of practical knowledge to be derived from the tests, those performed under full service conditions are by far the superior type, in that exact performances of a particular piece of equipment become known. However, this type of test must of necessity be expensive and time consuming. The time necessary for the test must be as long as the life of the equipment or at least for a period long enough that the practical use of the equipment is indicated. Duplicates of the items tested must be made of as many materials as are necessary to include those which are satisfactory, although previous knowledge may somewhat narrow this field. From the theoretical standpoint, such tests do not attempt to define or evaluate the probable mechanism of the corrosion reaction. These tests do, however, eliminate the necessity for the control of a great many variables which may be present should the equipment be tested in another manner.

Laboratory testing has therefore found a large variety of application in the field of corrosion studies, and many tests have been devised to fit a multitude of conditions. Borgmann[15] classifies these tests into five categories:

1. To study the mechanism of the corrosion.
2. To select the most suitable material for withstanding a definite environment.
3. To develop new alloys.
4. To determine environments in which a given material may be satisfactorily used.
5. To serve as a control test for the achievement of uniformity of a product.

The widest variety of laboratory tests are those designed to study the mechanism of a corrosion reaction. These, as a rule, are artificial in nature in order to control a particular variable for which the test is designed. While they do lead to a better understanding of the corrosion mechanism, the practical results may be misleading due to the conditions imposed by the test. Methods of measurement are varied, but are usually of such nature that the tests can be held to extremely close limits.

In the past several years, laboratory tests known as accelerated corrosion tests have been used. These tests are designed to give information as the behaviour of materials under service conditions in a relatively short time. In general, these tests have been unsuccessful in that certain factors must be intensified in order to cause measurable amounts of corrosion in short time intervals. This introduces conditions which are not comparable to those encountered in service. Some of these tests are the salt spray test, the acid immersion test, and the simulated atmosphere test. There are literally hundreds of other tests described in the literature of corrosion which are designed to meet a particular set of conditions.

The most common methods of reporting corrosion deal with the effect upon the metal corroded. Perhaps the most widely used is the loss of weight of the metal sample. This may be measured in units of weight per unit of time, or units of weight per unit of surface exposed. There are several objections to this, one being the necessity for removal of any corrosion products in order that the metal specimen may be accurately weighed. This type of testing ordinarily necessitates the use of a great many specimens, which must be exactly similiar in all respects, in order to gain information on the time-rate of corrosion.

A second method of measurement in the gain of weight of the metal specimen and this is usually reported in a manner similiar to that described above. This also has several objections. It is necessary to analyze the apparent corrosion product in order to determine the loss of metal. It is easily possible that all corrosion products do not remain firmly fixed on the specimen and loss of any of the material would give erroneous results. The amount of moisture from solutions contained in the corrosion products may vary, and unless careful procedures are followed, this may give a false result. In neither this method nor the one previously cited are special methods of attack measured.

A third and perhaps even more difficult method of measurement commonly used in the depth of pitting of the specimen caused by corrosion. This is, at best, difficult to obtain with accuracy, and again, in order to obtain time-rates a great number of specimens must be used.

While these are by no means all of the possible means of measurement of corrosion of the metal specimen itself, they are the methods most commonly used. Burgmann[15] lists sixteen general methods by which measurements may be taken without delving into the ramifications possible within each.

In the methods of testing and measurement discussed thus far, the effect of the environment upon the metal sample tested is the factor which is measured. Another type of testing, and the one which has been used in this work, is the effect of the metal upon the environment. This type of test gives valuable information on the manner in which the corroding agent is consumed in the corrosion process. With proper control, information about side reactions, the order of reaction with regard to the corroding medium, and the possibility of variances in rate during the process, may be obtained. This method has not been greatly used in the past and a good evaluation of the method as compared to the more common methods is not available. One objection that has been made is that it does not give much information as to the mechanism of the attack upon the metal itself. While this is quite possibly the case in so far as quantitative measurements are concerned, it would seem that qualitative evaluation with regard to pitting and area of attack should be as readily available with this method as with many others. In the past, the analysis of a corroding medium for a desired constituent has been tedious and in some cases almost impossible due to the difficulty in detecting small concentrations of a substance with accuracy and precision. This is particularly true when the changes in the concentrations of the desired constituent lie within the limits of error of the analysis. It has also been necessary to use many specimens in order to establish a rate of corrosion since it is necessary to destroy a particular reaction in order to measure the concentration of the constituent at any particular time.

By application of the polarographic technique, most of these objections have been overcome. It is readily feasible to make successive measurements of minute quantities of a constituent in a solution with satisfactory accuracy and precision. Kolthoff and Lingane[16] state that the accuracy of the polarographic method is of the order of plus or minus two per cent within the concentration range 10^{-2} and 10^{-4} molar, and plus or minus five per cent between 10^{-4} and 10^{-5} molar. This compares very favorably with the accuracy of other micro-analytical methods.

Essentially the polarograph is an instrument which permits a qualitative and quantitative analysis for the constituents of a solution by means of measured reduction currents resulting from the application of gradually increasing cathodic potentials to a dropping mercury or rotating platinum electrode. A cathodic wave is recorded by one of several means, the abscissa being the applied electromotive force, and the ordinate the current passing through the cell. The height of the wave thus recorded is a measure of the limiting diffusion current of the ion or molecule being measured and therefore of the concentration of the substance. The reduction potential of the substance, which is the point at which the wave is recorded, is characteristic of that ion or molecule. Substances having reduction potentials of from 0.0 volts to -2.4 volts with respect to the saturated calomel electrode may be determined in this manner.

The quantity of a substance reduced in a polarographic analysis is so small compared to the bulk concentration of the same material that any changes in concentration due to the analysis may be disregarded for any range in which the instrument is usable. Thus, successive analyses of the same solution may be made at intervals as rapidly as the limits of the mechanical factors of the instrument permit. For a hand operated machine from which only a quantitative analysis is desired, it may be possible to complete the determination within ten seconds for each run desired. For the total range of a camera recording machine such as the Sargent-Heyrovsky Model 12, three to five minutes are necessary, although it is rarely necessary to utilize more than one third of the possible voltage span. It is thus apparent that if the desired substance may be determined polarographically, this method is ideal for the establishment of a time-rate curve since the solution is not changed by the analysis.

Burns[17] suggested the use of the polarograph in corrosion studies of soluble metal ions such as lead. He, in 1937, compared the rates of the solution of two grades of lead in distilled water by measuring the rates polarographically. It is well to note here that since many metal ions are reducible at the dropping mercury electrode, it should be possible, in many cases, to measure the concentration changes of such ions appearing in a corrosion process.

The first use of the polarograph to study changes in the corroding medium was made by Van Rysselberghe[18] and his co-workers at the University of Oregon in connection with Office of Naval Research Projects in which the roles of oxygen and carbon dioxide in the corrosion process were sought. Reports of this work were published in 1948.[19] This article was published *in toto* in *Corrosion*[20] in 1950 because of the intense interest in this type of test.

Kittelberger and Elm[21] have used a modified form of polarographic analysis to determine the effect of various aqueous solutions upon the reactions at pure iron anodes. It is questionable that this work is strictly polarographic in nature, as the term is ordinarily employed, in that iron cathodes and anodes were used and therefore the curves obtained are not comparable to those commonly encountered. It should probably be defined as voltammetry as discussed by Kolthoff and Lingane.[22]

Further work using the polarographic method of studying changes in the corroding media is being undertaken at the present time under contracts with the Office of Naval Research at the University of Oregon.[23]

There are certain objections to the polarographic methods of study which should be pointed out. Since the method is micro-analytical in nature and the volume of the solution used is ordinarily less than fifteen milliliters, it is difficult is realize the ratio of test solution to area of the metal specimen which is recommended for laboratory tests by some investigators. Wesley[24] recommends that this ratio by four liters of solution per square decimeter of metal sample for simulated service tests. This would necessitate a metal surface of approximately 0.04 square centimeters in a fifteen milliliter cell. Obviously, errors in measurement of sample size are readily possible if this were followed. Consequently, if this ratio must be exceeded, erroneous information due to accentuated conditions must be recognized if a service comparison is desired. With extremely small samples, non-homogeneity of any portion of the metal will appear in a manner out of proportion to the true picture of the over-all corrosion. An objection to any test which must be carried out in a restricted volume, is that the rate of corrosion in such a volume often varies greatly from that when an unlimited supply of the corroding medium is available. Hence, information derived in one case is not strictly applicable in all others.

However, the rapidity with which the polarographic tests may be run, the accuracy and precision of the analytical method, and the large amount of information which may be obtained, give a definite place in the study of corrosion mechanisms to this procedure.

Whatever the method used in corrosion testing, the goal is measurement is reproducibility of results. For this reason, preparation of the sample to be tested is of great importance. Factors which must be closely controlled are the cleanliness of the sample, the size of the sample if comparisons are to be made, the presence and nature of surface films, the condition of the surface with regard to pitting and smoothness, and the homogeneity of the surface of the sample. Knapp[25] gives an excellent discussion of the methods of preparation of a metal sample for weight loss tests. The procedures which he illustrates, in general, are the same for any laboratory corrosion test.

The manner in which the sample is presented to the corroding medium must also be strictly controlled. For this reason standard methods of testing have been evolved. The American Society for Testing Materials has published a great number of these in various bulletins, monographs, and journal articles. Another series of standard tests are to be found in Federal Specifications for testing materials. Many of the technical societies have also published standards for corrosion tests for various materials in which they have a particular interest.

Corrosion by Sulfur Dioxide

In 1948, Doctor I. A. Denison,[26] chief of the Underground Corrosion Section of the National Bureau of Standards, suggested to

Doctor Armin H. Gropp of the University of Florida, that since little is known of the corrosion process when compounds of sulfur are present, a polarographic study of such a process would be of value.

Since there are a great number of sulfur compounds which may take part in the corrosion process and an almost unlimited number of metals and alloys which might be affected, the suggestion was refined to include only one of the greater offenders, sulfur dioxide, with pure iron and a series of ferrous alloys.

Tests on sulfur dioxide corrosion have been divided into two predominate groups; those at elevated temperatures, and those in solution and in the atmosphere at ordinary temperatures. Discussion will be restricted to the latter group to confine the topic to the subject of this work.

Thompson[27] states that in the case of atmospheric corrosion, sulfur dioxide is the predominate corroding agent. Clarke[28] shows that sulfur dioxide is the chief constituent of the air which affects indoor corrosion and shows that it readily corrodes steel and nickel when the relative humidity is over seventy per cent. Tolley[29] has also shown that the presence of water vapor with sulfur dioxide increases the corrosive effect. Karnitskii and Golubev[30] have shown that in sulfuric acid and hydrochloric acid solutions containing dissolved sulfur dioxide, the corrosion is proportional to the concentration of the sulfur dioxide. Klinov and Andreeva[31] have shown that chromium-nickel, and chromium, nickel, and manganese steels are resistant toward moist sulfur dioxide but that other metals are attacked. The *Corrosion Handbook*[32] indicates that ordinary iron and steels are not suitable for use with either moist sulfur dioxide or sulfurous acid, but that certain special alloys may be used. Speller[33] states that sulfur dioxide fumes from sulfur burners may be handled in cast iron without undue corrosion so long as the temperature is high enough to prevent condensation of moisture and resultant liquid sulfurous acid, but that lead must be used if this is not feasible.

It is then apparent that a problem exists in that the presence of sulfur dioxide in solutions and in moist atmospheres accelerates the rate of corrosion of most metals, but that apparently little is known of the reason for this behaviour. It is beyond the scope of this work to determine if it is possible to differentiate between moist sulfur dioxide and aqueous solutions of sulfur dioxide, but the author feels that in the absence of evidence to the contrary, the behaviour must be essentially the same in either case.

The Polarographic Reduction of Sulfur Dioxide

Gosman and co-workers[34] first showed the possibility of reducing sulfur dioxide at the dropping mercury electrode and obtained well defined waves in one-normal hydrochloric acid. They further showed that no reduction occurred in neutral or alkaline solutions. Kolthoff and Miller[35] extended this work and showed that while sulfur dioxide is readily reduced in acid solution, the wave height found was dependent upon the pH of the solution, and that with constant concentration of the sulfite or sulfur dioxide, it decreased with increasing pH. In strongly acid solution only one wave was found, but at a pH of six two small waves appeared. No reduction occurred at a pH greater than six. The half wave potential in one-normal hydrochloric acid was found to be -0.2 volts with respect to the saturated calomel electrode although this varied with the supporting electrolyte.

Gosman and his co-workers[34] assumed that the wave found in acid solution was due to the reduction of the sulfur dioxide to the hyposulfite ion:

$$2\ SO_2 + 2\ e \rightarrow S_2O_4^{=}$$

Kolthoff and Miller[35] could not confirm this and postulated that two electrons are required for the reduction of one molecule of sulfur dioxide and that sulfoxylic acid is formed:

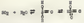
$$SO_2 + 2\ H^+ + 2\ e \rightarrow H_2SO_2$$

They obtained a calculated diffusion constant from their data which was in agreement with the theoretical value for a two electron reduction.

In order to explain the phenomenon of decreasing wave height with increasing pH, Gosman[34] assumed that sulfurous acid is reduced and that an extremely slow equilibrium exists:

$$H^+ + HSO_3^- \rightleftarrows H_2SO_3$$

Kolthoff and Miller[35] believe this to to an implausible explanation, since in the electrodeposition of hydrogen at the dropping mercury electrode from solutions of weak acids, the attainment of the dissociation equilibrium is found to be faster than the speed of the electro-reduction. They postulate that sulfurous acid, like phosphorous and nitrous acids, exists in tautomeric forms:



$$SO_2 + H_2O \rightleftarrows \mathrm{HO{-}S({=}O){-}OH} \rightleftarrows \mathrm{HO{-}SH({=}O){=}O}$$

(I) (II)

Form I is the weaker acid of the two and is reducible whereas form II is stronger and oxidizable.

They then assume that at intermediate pH values, in the neighborhood of pH three for example, most of II may be present in the ionized form and I present, for the most part, in the un-ionized form. Thus, at such a pH only a small fraction of the total sulfur dioxide may be present as form I and the greater part as form II. Since they consider only I measured by the polarograph, this may result in a smaller wave for a given concentration of sulfur dioxide than when the equilibrium is such that more is present in the reducible form. With increasing pH then, that fraction of the sulfur dioxide present as form I increases, and depending upon the equilibrium constant giving the ratio between I and II, and the hydration constant of sulfur dioxide, most of the sulfur dioxide may be found in form I in strongly acid media. If form I (ionized and un-ionized) is reducible at the dropping mercury electrode and the speed of transformation of II to I is relatively small, it is evident that the height of the wave should be dependent upon the pH, unless the dehydration of sulfurous acid in sulfur dioxide is acid catalyzed.

It must be noted here that Kolthoff and Miller[35] obtained sulfurous acid by adding solutions of sodium sulfite to strong acid or buffer solutions to cause the formation of sulfur dioxide. In preliminary work for this problem, it was felt that the easiest way to obtain known concentrations of sulfur dioxide would be to add measured concentrations of reagent grade sodium bisulfite to a buffered acid solution in the pH range desired. This was abandoned when it was found that when this procedure was followed in acetate and citrate buffers in the neighborhood of pH 5, the wave height gradually increased with time until a maximum was reached several hours after the original addition of the bisulfite. This was not the case when gaseous sulfur dioxide was bubbled through the solution, the maximum wave height occurring immediately. Evidently some equilibrium concerned with a form of sulfur dioxide which is measured must be attained. The author is not prepared to state at this time whether this is because the reaction between the sulfite or bisulfite and the acid buffer is relatively slow, or whether this reaction is rapid, and the attainment of a measurable form is slow, and is of the order postulated by Kolthoff and Miller. Since a method of obtaining a known concentration of sulfur dioxide in solution more suited to the needs of the problem was found, no further work was done on the subject. It is to be hoped that this may be done at some future date. The method used, and the results obtained by its use, will be discussed in a later section of this dissertation.

It must be emphasized that the reductions of sulfur dioxide so far discussed pertain only to the reductions at the dropping mercury electrode in the analysis of this compound. They may not be those which pertain to the reduction of sulfur dioxide in the corrosion process and may, in fact, have little to do with these mechanisms.

Statement of Problem

A study of the corrosion of several iron and steel alloys in an environment containing sulfur dioxide has been undertaken. Particular emphasis has been placed upon the initial phases of the corrosion and upon the rates of corrosion with special regard to changes in these rates. It was hoped that some contribution could be made with regard to possible mechanisms of the sulfur dioxide problem concerning which little except empirical data are available.

CHAPTER II

EXPERIMENTAL PROCEDURE

A Sargent-Heyrovsky Model XII photographically recording polarograph was used for this work. The circuit for this instrument is shown in Figure 1. Information concerning the mechanical construction and sensitivity of the polarograph is contained in the instruction pamphlet for the machine.[36]

The cell used is shown in Figure 2. The essential difference between this cell and those commonly used in polarographic work is the addition of a glass barrier at the bottom of the cell to restrict the anode pool and to allow the placing of metal samples in such a position that corrosion products could not contaminate the anode. It was found that such products, when allowed to come in contact with the anode, caused a shift in potential such that measurements of the diffusion current and the half-wave potential could not be made. The metal samples were bent to such a shape that they could be fitted between the glass barrier and the outer wall and rested on edge on the bottom of the cell. It was found that the presence of the barrier did not affect diffusion appreciably in that stirring the contents of the cell by gentle shaking gave no perceptible difference in the wave height of the sulfur dioxide.

The use of other cells was tried without success. It was thought that an "H" cell with the metal sample in one arm and the anode in the other would be the most suitable apparatus but this was found to be unsatisfactory in that homogeneity of the solution could not be obtained after the corrosion process had begun.

It was found that the use of rubber in contact with the solutions used caused a loss of sulfur dioxide. Consequently ground glass fittings were used throughout the system. The capillary was sealed into a ground glass stopper by means of "hard" De Khotinsky cement, and the same capillary was used throughout the work. Whenever the capillary became dirty it was cleaned by drawing several drops of twelve-molar nitric acid through the bore, followed by distilled water and air drying. Glass tubing was used in place of the rubber tubing commonly employed between the cathode reservoir and the capillary. This was fitted with a stop-cock in order that the flow of mercury could be interrupted as desired.

Two cells were used, both having a volume of twelve milliliters. Both cells were calibrated for loss of sulfur dioxide either by loss from solution or by use by the components of the cell. The results of such a calibration are shown in Figure 3. It was demonstrated that if the ground glass stopper was properly inserted into the cell there would be no loss of sulfur dioxide for a period much longer than that required for this work.

The first cell adopted for use was calibrated for wave height of the sulfur dioxide for known sulfur dioxide concentrations by analyzing the contents of the cell as well as duplicate portions of the solution with which the cell had been filled. The official method of the American Public Health Association[37] was used for this analysis. It is based upon the reduction of a standard iodine solution by the sulfur dioxide solution followed by back titration with standard thiosulfate solution. The second cell was calibrated against the first by determining the wave heights for portions of the same sulfur dioxide solution in the two cells. This was necessary since the wave height was dependent upon various factors which were in turn dependent upon the capillary used. Calibration curves for the two cells were then constructed. These are shown in Figure 4.

A galvanometer shunt ratio of 50 was used in all work. This corresponds to 0.2450 micro-amperes per millimeter of wave height. It was found that a lower sensitivity would not cover a concentration range wide enough for the construction of a good calibration curve or give the required sensitivity of analysis. The first objection was also true of a greater sensitivity, as well as the fact that the sensitivity of the chemical analysis used for calibration was not as great as that of the polarograph, and thus calibration curves as constructed were of little value.

Using the galvanometer shunt ratio of 50, a concentration range of between 15 and 150 parts per million of sulfur dioxide could be adequately covered. Although measurements of wave height for concentrations below 15 ppm could be made using this sensitivity, it was felt that this was not advisable. As has been mentioned previously, the accuracy of the chemical analysis was not good at a very low sulfur dioxide concentration. Polarographically, it was possible to detect differences as small as two parts per million in the sulfur dioxide in any concentration range, but below five parts per million the precision of the wet analytical method was such that the results of analyses could not be considered valid.

Previous work[35] on the polarographic analysis of sulfur dioxide indicated that the wave height for a given concentration of sulfur dioxide varied with the pH of the solution between a pH of one and a pH of six. By comparison of one-tenth molar potassium chloride solutions and citrate buffer solutions of exactly equal sulfur dioxide concentrations, it was found that there was no measurable variation in the wave height between a pH of 2.15 and a pH of 4.00. Above the latter pH there was a definite difference in the wave height, that of the buffered solutions always being lower. Comparisons were made in increments of 0.2 pH units between pH 2.15 and pH 4.50. Polarograms of some of these comparisons are shown in Figure 5.

Table 1, page 24, shows the pH of a series of one-tenth molar potassium chloride solutions of varying sulfur dioxide concentration. From this it can be seen that below 15 ppm of sulfur dioxide, the pH would be such that the wave height might be affected. It was found that the pH of the corroding solutions remained below pH 4.0 so long as more than 15 ppm of sulfur dioxide was present, although it was, in most cases, higher than the corresponding concentration of sulfur dioxide would indicate.

All pH measurements were made with a Beckman Model G pH meter which was standardized in the proper range before each set of measurements.

One-tenth molar potassium chloride was used as the supporting electrolyte in order that the primary corrosion of the iron samples might be restricted as far as possible to the action of sulfur dioxide and not to hydrogen displacement as would have been possible had a strong acid been used. The supporting electrolyte was made up in five liter quantities from reagent grade potassium chloride dissolved in distilled water which had been boiled for several hours to remove oxygen. The solution was kept free from oxygen by bubbling continuously with tank nitrogen.

TABLE 1

pH OF 0.1 MOLAR SOLUTIONS OF HCL CONTAINING SO_2

SO_2 in ppm	pH
135	2.89
95	2.98
70	3.11
57	3.25
44	3.39
15	3.90

It was necessary to keep all solutions free from oxygen since the sulfur dioxide was readily oxidized and, in addition, the first half-wave potential for oxygen lay so close to that for sulfur dioxide that measurement of the latter could not be made accurately when the former was present.

A stock sulfur dioxide solution was made by bubbling tank sulfur dioxide into an oxygen-free solution of one-tenth molar potassium chloride. This solution was maintained under a nitrogen atmosphere at all times, and was measured for use by means of a five milliliter burette which was connected to the stock reservoir by means of a siphon. Air was excluded from the burette by means of a thin rubber bulb which had been flushed with nitrogen and which allowed pressure differentials when filling and using the burette.

The metal samples used in this work were supplied by Dr. R. B. Mears of the Carnegie-Illinois Steel Corporation, and Dr. I. A. Denison of the National Bureau of Standards. All samples, with the possible exception of the "pure iron" furnished by Dr. Mears, were of steels which had been used in corrosion tests by the two organizations, and provided a good sampling of the common low-carbon industrial alloys. The "pure iron" was made from especially selected low metalloid scrap and pig iron by the open hearth process, and with the exception of re-melted electrolytic iron, was probably as pure as could be obtained.

The metal test specimens were cut to a width of one centimeter and a length of two centimeters, with the exception of the pure iron which was slightly smaller to account for a difference in thickness. All specimens had a surface area of between 4.35 and 4.50 square centimeters. Since the primary objective of this investigation was not to make an exact comparison between samples, it was believed that the small difference in surface areas would not be critical.

All specimens, with the exception of the "pure iron" were annealed for one-half hour at 950° C. in a small electrically heated muffle furnace. This was followed by cooling in the furnace. Although an examination of a number of standard corrosion tests indicated that no special heat treatment procedure was used in such tests, it was felt that in the present study the ratio of the surface of the edges to the total surface was relatively large and that strains caused by the cutting of the samples would have an undue effect unless removed in some manner. It was realized that bending the sample after the annealing process would again introduce a certain strained condition in the metal, but it was felt that this would be relatively small as compared to that due to unrelieved sheared edges. It was also felt that such strain, while affecting the corrosion rate, would not change the manner in which the corrosion occurred.

The scale was removed from the sample by wire brushing and the samples polished with successive grades of emery cloth. After the polishing had been carried to 2/0 abrasive, the sample was bent to the final shape, and a final polish applied with 3/0 emery cloth. This final polishing was not done until the sample was to be used.

Immediately before use, the sample was thoroughly washed with distilled water and then with 95 per cent alcohol to remove grease from handling. A final wash with distilled water followed. All specimens which would not give an even film of water on washing were re-scrubbed with alcohol until satisfactorily free from grease. The sample was then dried by blotting with filter paper.

No attempt was made to achieve either the optimum or the minimum sample condition for corrosion, but rather to achieve a condition wherein many of the factors which might affect the corrosion would be known.

After the sample had been prepared as previously described, it was placed in the cell in which it was to be used. The glass stopper for the cell which contained the capillary was a permanent part of cathode reservoir. The cell was clamped in a position such that the stopper was partially within the ground glass neck of the cell but did not completely close the apparatus. Nitrogen was then continuously passed through the cell until the solution was introduced. The connection to the nitrogen tank was made through the anode arm of the cell.

The solution was then prepared in a glass stoppered volumetric flask. The flask was thoroughly flushed with nitrogen and then a small volume of the stock sulfur dioxide solution was introduced from the burette in such a manner as to prevent access of air in so far as possible. Enough of the oxygen-free supporting electrolyte was added to bring the total volume of the solution to the desired quantity. The usual proportions were from five to ten milliters of the sulfur dioxide solution per 100 milliters of total volume depending upon the concentration desired. The flask was stoppered after the space above the solution had again been flushed with nitrogen.

The mercury for the anode was then introduced into the anode arm of the cell by means of a pipette. Two to three milliters was required. Following this, the solution was poured into the cell, in excess, through the partially open cell top. The cell was raised and rotated to close the apparatus, care being taken that no space was allowed to exist between the solution in the cell and the stopper, and that a good seal was obtained. The first measurement of sulfur dioxide content was made immediately.

The same procedure was followed in the calibration of the cells with the metal sample being omitted.

The flow of the mercury from the cathode was interrupted after every measurement by means of a stopcock in the reservoir line. As the number of measurements increased, the mercury in the anode would back up in the anode arm, allowing the volume of the solution to remain constant. Whenever the mercury level in the anode arm extended above the level of the anode surface within the cell, the excess was removed by means of a small pipette.

The usual interval between measurements was one-half hour, although this varied. It was found that this was often enough to show concentration changes as they occurred. Any variations from this interval are shown in the figures to be discussed later.

The total time which was measured for each run was usually twelve hours. In order to obtain the interval between twelve and twenty-four hours, the apparatus was placed in operation as previously described and an initial measurement made. The mercury flow to the capillary was then interrupted and the cell process allowed to continue with no further measurements for twelve hours. The changes in the wave height were then measured at regular intervals after this time.

Measurements of wave height were made at the half-wave potential in all cases, using standard techniques. These measurements were made to the nearest one-half millimeter which corresponded to one part per million of sulfur dioxide at the sensitivity at which the apparatus was used.

It was noted that apparently some charge accumulated after a corrosion cell containing the metal sample had been in operation for six to eight hours. Although the distance between the residual current line and the diffusion current line remained the same, the slope between these lines became extremely erratic and appeared to be almost of the same nature as that when a capillary became foul. However, by allowing the mercury stream to continue and applying the full potential of the polarograph across the cell for several seconds, this phenomenon disappeared, and the usual wave could be recorded.

No explanation for this behavior will be attempted in this discussion. There does not appear to be an instance of a similiar phenomenon recorded in the literature, but it is believed that a plausible explanation may be found in the properties of mercury in various electrolytes as discussed by Kolthoff and Lingane.[38]

CHAPTER III

DISCUSSION AND INTERPRETATION OF DATA

The data obtained in this work are shown in Figures 6a through 17 and in a general summary given in Table 3. The information is shown graphically in curves showing the consumption of sulfur dioxide by the various samples used. These are plotted in parts per million of sulfur dioxide remaining at one-half hour intervals for twelve hour periods. It was felt that the use of the concentration designation "parts per million" would be more consistent with industrial usage and fully as clear as any method which might be used.

Although curves are shown for twenty-four hours, the primary concern of this investigation was the initial phase of the corrosion reaction. The last twelve hours are included only to give general information as to the nature of the process during this time. It is felt that much more time than twenty-four hours should be studied if the total picture is desired. For this reason the curves for the first twelve hours must be considered to have the greatest significance in the discussion to follow.

The figures are arranged to show the metal samples in order of increasing alloy content, beginning with the "pure iron." Two twelve hour periods are shown for each sample, these being placed in successive order for convenience.

Since the concentration of the sulfur dioxide solution in the stock reservoir varied slightly from day to day, it was extremely difficult to obtain exactly similiar solutions for the duplication of a corrosion process. It was demonstrated, however, that the same general process occurred in the corrosion when the initial concentration of the sulfur dioxide differed in several solutions used with the same metal sample. This is shown in Figures 14, 15 and 16.

Figures 6a and 6b show the consumption of sulfur dioxide by "pure iron." The initial rate of consumption is high and persists for almost two hours, after which an inhibiting action takes place, and the rate is extremely slow for a two hour period. At the end of this time, there is a sharp increase in the consumption of the sulfur dioxide, again for two hours, and again followed by a period of inhibition. This lowered activity lasts only a short time and the rate again increases, this time for about three hours, after which a third period of inhibition sets in. Figure 6b shows that the general picture of the process from twelve to twenty-four hours is much the same, although the overall rate is greatly decreased.

Figures 7a and 7b show the consumption of sulfur dioxide by sample C 409, a low carbon steel with very low alloying elements. Again, the initial two hour period shows the greatest rate of consumption of the corroding agent. This is followed by decreased activity for two hours, and then an increased rate of consumption. This increased rate continues for more than four hours when a second period of inhibition occurs. after approximately another two hours, the rate again increases. However, there is almost continuous consumption of sulfur dioxide for the entire twelve-hour period, although the rate is much less than that for pure iron.

The consumption of sulfur dioxide by sample 03, which is also of low alloy content, is shown in Figures 8a and 8b. It contains a relatively large percentage of copper. The greatest rate of consumption of sulfur dioxide is in the first two hour period and this is also followed by a lower rate for the next two hours. After this, the sulfur dioxide is consumed at the same rate for successive two hour periods up to twelve hours, although the curve shows short periods of inhibition at regular intervals. The last twelve hours shows three periods of increased activity and three periods of inhibition. The rate of consumption of sulfur dioxide appears to increase during this period.

Figure 9a and 9b give information on sample 01 which is slightly higher in alloy content than sample C 489, although of the same general composition. It contains the highest percentage of manganese of any of the samples tested. The curve obtained for this steel is quite similar to that obtained for sample C 489 with periods of activity and inhibition. As before, the greatest rate of consumption of sulfur dioxide occurs in the first two hours and again this is followed by a period of inhibition. The rate for the first twelve hours appears to be roughly divided at approximately six hours. The rate for the last six hours is slightly greater than that for the first six, since the first period of inhibition lasts for almost four hours before activity increases. The last twelve hours also show periods of increase in activity. This curve is almost straight in nature, but it can be seen that the last ten hour period should be indicated as two periods with a change in slope at about twenty hours.

Figures 10a and 10b are for sample C 19. This sample was the highest in phosphorous, silicon, and copper of any of the alloys tested. It does not show an inhibition period until after the sixth hour although the rate is somewhat less after the first two hours. The inhibition period is short, lasting only about an hour. The consumption of sulfur dioxide is then resumed without another inhibition period, although the rate varies and is not constant. The last twelve hours show pronounced periods of activity and inhibition.

Sample C 029 is shown in Figures 11a and 11b. This sample contains 2.1 per cent of nickel. Again in the first two hours the consumption of sulfur dioxide proceeds at the greatest rate. After this a period of inhibition occurs for two hours, followed by a two hour period of increased consumption. This is followed by three hours of inhibited action, and then again, increased activity on the part of the sample. The final twelve hours is marked by alternate periods of activity and passivity, four periods of each being shown.

Figures 12a and 12b show the results for sample 246 which contains 3.5 per cent of nickel. In the first twelve hours, the periods of activity and passivity are well defined as compared to the previous sample. Four periods of activity and three periods of inhibited action are to be observed. In the final twelve hours, the differentiation between the first periods of activity and inhibition is less well-defined, but is readily apparent. At the eighteenth hour there is a sharp increase in the rate of sulfur dioxide consumption which ends in a period in which no sulfur dioxide is consumed for almost three hours. Activity begins again after this period.

Sample 25369, containing 5.9 per cent of chromium, is shown in Figures 13a and 13b. This type of steel is usually known as 4-6 Chromium alloy. The first two hours show a rapid consumption of sulfur dioxide and are followed by a three hour period in which there is apparently no use of the corrodent. A two hour period of activity is then followed by a two hour period of complete inhibition. Increased activity is again resumed at the eighth hour and continues for the rest of the twelve hour period. The last twelve hours assume an almost steady rate of sulfur dioxide consumption with two short periods of inhibition between the sixteenth and the twentieth hours.

Figure 14 shows the relation between the time-rate curves for three different concentrations of sulfur dioxide when used with sample 25369. It may be seen that the curves are very similiar and that periods of activity and inhibition occur in the same manner for each run. It is apparent that curves one and three are very similiar, and that, with the exception of the first hour, curve two differs little from the others.

Figure 15 gives the same information for sample C 469. In this case, although the time studied was much shorter, it can be seen that there is a period of rapid consumption of sulfur dioxide followed by a period of almost complete inhibition. Curves two and three indicate that this is followed by an increased rate of consumption. Although information was obtained to show that there was also an increased rate of consumption of sulfur dioxide in the process shown in curve one following the period shown, too few observations were made after the sixth hour to show exactly how this occurred.

Figure 16 shows duplicate runs for sample 63. A period of six hours is covered. In this case, it can be seen that there is almost exact duplication in the nature of the consumption of the sulfur dioxide.

Table 3, page 64, summarizes the information obtained for the first twelve hours for each sample. While the general corrosion picture is depicted, that of periods of activity followed by periods of inhibition, reference to the curve for a particular sample gives a truer picture of the corrosion process. In all cases, it is seen that the greatest consumption of sulfur dioxide by the sample occurred during the first two hours.

The logarithm of the remaining sulfur dioxide concentration versus the time is plotted for three samples in Figure 17. If the logarithm of the concentration of a component of a reaction is plotted against time during the period in which the reaction is taking place, a straight line will result if the reaction is of first order with respect to that particular component.

It can be seen that the corrosion process, therefore, is of first order with respect to the sulfur dioxide, for at least the greater portion of the first twelve hour period. Only plots for samples 25349, C 489 and 63 are shown. Two of these represent the extreme limits of the rates found, and the third represents a sample rate falling between these limits. All others studied gave the same type of plot, the slope of the line being the only major difference.

It was noted that when the cells were cleaned at the end of a corrosion period, hydrogen sulfide appeared to be present. When samples of metal were placed in a stronger sulfur dioxide solution than those which were used for corrosion tests, the odor of hydrogen sulfide became very strong in a short time. Apparently then, sulfur dioxide is reduced either wholly or in part to the sulfide ion. Dr. L. A. Dennison[39] of the National Bureau of Standards has stated that he is of the opinion that many sulfur compounds may be reduced to the sulfide, or to some polysulfide, during a corrosion process. In addition to the odor of hydrogen sulfide, it was noted that in this work the samples became coated with a black deposit. Simple qualitative tests showed this to be a sulfide, and apparently ferrous sulfide. These observations apparently confirm the statement of Dr. Dennison.

It was also noted that, although the solutions used were acid and had a pH of less than 4.0, no measurable quantity of hydrogen was evolved during the corrosion process.

Any mechanism for the corrosion which may be postulated must therefore account for the presence of the sulfide and the lack of evolution of hydrogen gas in the acid solution.

The most probable mechanism is that of the reduction of the sulfurous acid by the iron to give the sulfide. Using oxidation potentials from Latimer,[40] the following reactions and values may be calculated:

$$3\ Fe \rightarrow 3\ Fe^{++} + 6\ e \qquad E_0 = +0.44\ v.$$

$$3\ H_2O + S^{=} \rightarrow H_2SO_3 + 4\ H^{+} + 6\ e \qquad E_0 = -0.13\ v.$$

$$3\ Fe + H_2SO_3 + 4\ H^{+} \rightarrow 3\ Fe^{++} + S^{=} + 3\ H_2O \qquad E_0 = +0.57\ v.$$

By the use of the equation $\Delta F_0 = -nFE$, it may be calculated that ΔF_0 for the above reaction is -78.9 kilocalories. This is certainly large enough for the reaction to be readily possible.

This reaction would account for the presence of the sulfide which was found, and the black coating of ferrous sulfide on the metal sample. The rapid initial consumption of sulfur dioxide would be caused by the reduction of the sulfur dioxide and the consequent formation of a ferrous sulfide coating upon the surface of the sample. Then, as the coating upon the metal becomes thicker and more stable, access to the metal by further sulfur dioxide is denied. This would account for the period of apparent inactivity which has been shown to follow a period of sulfur dioxide consumption.

The equilibrium constants for hydrogen sulfide are given by Latimer[34] as 1.15×10^{-7} and 1.0×10^{-15} respectively. By combination of K_1 and K_2, the following expression is obtained:

$$\frac{[H^{+}]^2\ [S^{=}]}{[H_2S]} = 1.15 \times 10^{-22}$$

Latimer[34] gives the solubility product for FeS as 1.0×10^{-19}, so that the sulfide ion concentration must have the value $10^{-19}/C_{Fe^{++}}$. If this is substituted into the equilibrium expression for hydrogen sulfide, the equation becomes, $\frac{[H^+]^2 \quad 10^{-19}}{[H_2S]\ [Fe^{++}]} \doteq 1.15 \times 10^{-22}$

and, by rearrangement, the concentration of the ferrous ion must have the value:

$$[Fe^{++}] = \frac{[H^+]^2 \quad 8.7 \times 10^{2}}{[H_2S]}$$

In this work the pH remained below four, so if one takes this as a limiting value, and assumes that the molar concentration of the hydrogen sulfide approaches the maximum molarity obtainable if all the sulfur dioxide has been converted to the sulfide, or a value of 2×10^{-3} molar (128 ppm as sulfur dioxide), any ferrous sulfide can be re-dissolved until the ferrous ion concentration becomes approximately 5×10^{-3} molar. This is the extreme case; in any other case, which might be assumed, the ferrous ion concentration would be much larger since the pH would be lower, and, obviously, all the sulfur dioxide present cannot form hydrogen sulfide.

Thus it is possible that the ferrous sulfide coating upon the iron sample is dissolved in the acid media. If the rate of dissolution is slow, some time will elapse until the remaining coating becomes permeable, and sulfur dioxide can again react with the metal. When this happens, and the consumption of the sulfur dioxide is again resumed, a new period of increased activity is shown. The process then becomes cyclic in nature and continues to remain so.

The formation of the original ferrous sulfide coating must depend upon the relative rates of several reactions and at least two equilibria. The first of these is the reaction of the ferrous ion and the sulfide ion to form ferrous sulfide, and the equilibrium concerned with the dissolution of the ferrous sulfide. The other readily apparent reaction and equilibrium is that concerned with the hydrogen ion and the sulfide ion in the formation of hydrogen sulfide. It must be realized that the situation at hand is not analogous to the precipitation of ferrous sulfide by hydrogen sulfide in acid solution, as is the case in ordinary qualitative analysis. In that case, the sulfide ion must be formed by the ionization of hydrogen sulfide, and this is prevented by the hydrogen ion already present. In the present case, the sulfide ion is formed by the reaction at the surface of the iron sample. At the interface between the solution and the metal surface, a high local concentration of ferrous ion and sulfide ion exists, and the hydrogen ion concentration is diminished because of the reduction that takes place. The rate of reaction between the ferrous ion and the sulfide ion must then be more rapid than that establishing the equilibrium between the diminished concentration of the hydrogen ion and the sulfide ion, and the formation of ferrous sulfide results. The probability of this reaction must be considered since the ions are present in an interface between the solution and the solid metal sample and not in the bulk of the solution where the hydrogen ion-hydrogen sulfide equilibrium would be most effective.

The explanation of the role played by ordinary alloying elements in changing the rate of consumption of sulfur dioxide among the various steels is beyond the scope of this work, but it must be exceedingly complex. Other investigators[41,42] have shown that steels which are resistant to sulfur dioxide must contain large percentages of alloying element, usually chromium. This percentage must be so high that the surface of the alloy contains enough of the additional element so that reactions must be considered with regard to this element as well as the iron. In the case of chromium alloying, the minimum percentage of chromium considered necessary for corrosion resistance is approximately twelve per cent and may reach a value of thirty per cent depending upon the presence of additional elements such as nickel. It is assumed that such an alloy is resistant because of the formation of a film of oxide or adsorbed oxygen upon the surface so stable and tenacious that no attack by a corroding agent may proceed upon the surface of the alloy, and that the alloying element contributes to the nature of this film.

Although a mechanism for the corrosion of ordinary iron and steel alloys has been postulated which satisfactorily explains the data obtained, there is always the possibility that some other reaction, although less apparent, may actually take place. It is also quite possible that the corrosion process may involve several reactions operating concurrently.

The reduction of a solution of sulfur dioxide may yield a great many possible products. The two best known are the thiosulfate and free sulfur. No free sulfur was observed at any time in a corrosion cell. The half-wave potential of the thiosulfate ion is given by Kolthoff and Lingane[43] as -0.15 v. with respect to the saturated calomel electrode. Since this is within the range covered in the measurements of the sulfur dioxide concentration, the presence of any thiosulfate ion should have been apparent in the polarograms which were made. This was not the case, and no evidence was obtained to indicate the presence of this ion. It may be noted here that there is no recorded half-wave potential for a sulfur compound above that of sulfur dioxide in acid solution, and since no wave other than that of sulfur dioxide was observed between 0.00 volts and approximately -1.4 volts, it would seem that any sulfur compound which can be further reduced polarographically is not indicated. Since free sulfur could not be found by the use of the polarograph, the possibility that it may have been present as a transitory state in the reduction process, or in quantities as small as to escape visual detection, cannot be overlooked.

As has been mentioned previously, it has been suggested[39] that the products of the corrosion by sulfur compounds may be complex and consist of polysulfides as well as the simple sulfide. This must be considered since the values for the free energy of formation of the sulfide ion and the various polysulfide ions differ by relatively small amounts. Latimer[40] calculates the free energies as follows: S^{--}, 23,420 cal.; S_2^{--}, 23,100 cal.; S_3^{--}, 22,400 cal.; and S_4^{--}, 20,700 cal.

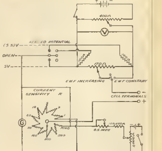


Figure 1.

Wiring diagram, Sargent Model XII Polarograph.

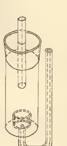


FIGURE 2

Polarographic Cell

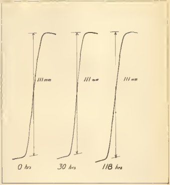


FIGURE 3

Polarograms of SO_2 at Various Times

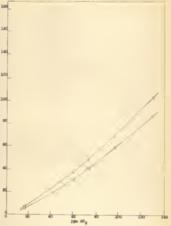


Figure 4.-- Calibration of Polarographic Cells

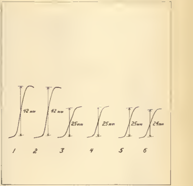


Figure 8.- (1) 0.1 M KCl containing 62 ppm SO_2, pH 3.15. (2) Citrate buffer containing 62 ppm SO_2, pH 3.60. (3) 0.1 M. KCl containing 44 ppm SO_2, pH 3.39. (4) Citrate buffer containing 44 ppm SO_2, pH 3.40. (5) Citrate buffer containing 44 ppm SO_2, pH 3.81. (6) Citrate buffer containing 44 ppm SO_2, pH 3.98.

TABLE 2

COMPOSITION OF IRON AND FERROUS ALLOYS

Sample Number	Composition, Per Cent							
	C	Mn	P	S	Si	Cu	Ni	Cr
Pure iron	0.02	0.04	0.006	0.020	0.002	0.007	0.006	0.001
C 489*	.04	.31	.008	.018	.011	.012	.01	.003
03	.03	.47	.07	.06	.003	.27	.03	.03
01	.04	.49	.07	.042	.008	.05	.01	.10
C 19	.09	.38	.11	.026	.72	.33	.03	.92
C 089	.13	.42	.010	.020	.21	.16	2.1	.13
246	.04	.46	.014	.027	.004	.06	3.5	.16
25369	.10	.40	.014	.024	.32	.028	.28	5.9

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*Sample designations are those of the Research Laboratory, Carnegie Illinois Steel Corporation, Vandergrift, Pennsylvania, from whom the analyses were obtained.

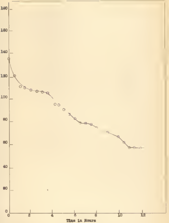

Figure 6a.— Consumption of Sulfur Dioxide by " Pure Iron "

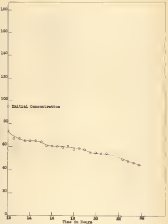

Figure 8b.— Consumption of Sulfur Dioxide by " Pure Iron "

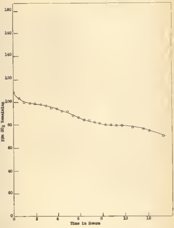

Figure 7a.— Consumption of Sulfur Dioxide by Sample C 488

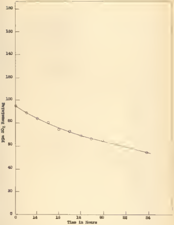

Figure 7b.-- Consumption of Sulfur Dioxide by Sample C 489

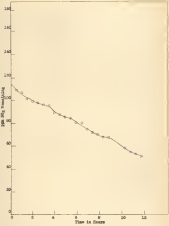

Figure 8a.-- Consumption of Sulfur Dioxide by Sample 03

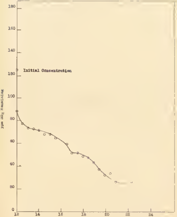

Figure 8b.-- Consumption of Sulfur Dioxide by Sample 03

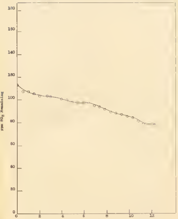

Figure 9a.-- Consumption of Sulfur Dioxide by Sample 01

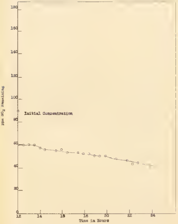

Figure 9b.-- Consumption of Sulfur Dioxide by Sample 01

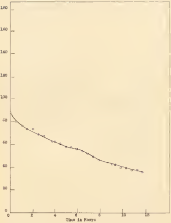

Figure 10a.— Consumption of Sulfur Dioxide by Sample C 19

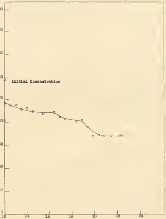

Figure 10b.-- Consumption of Sulfur Dioxide by Sample C 19

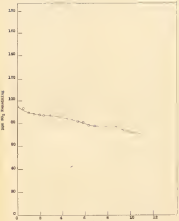

Figure 11e.-- Consumption of Sulfur Dioxide by Sample C 029

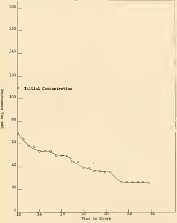

Figure 11b.-- Consumption of Sulfur Dioxide by Sample O C29

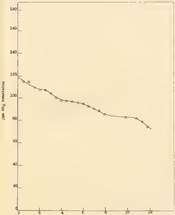

Figure 12a.-- Consumption of Sulfur Dioxide by Sample 246

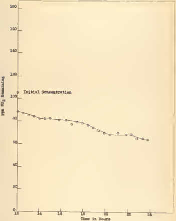

Figure 12b.-- Consumption of Sulfur Dioxide by Sample 246

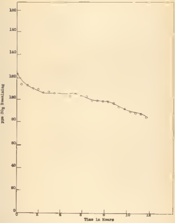

Figure 13a.-- Consumption of Sulfur Dioxide by Sample 25369

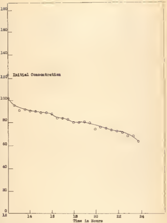

Figure 15b.-- Consumption of Sulfur Dioxide by Sample 25369

TABLE 3

PERCENTAGE OF TOTAL SULFUR DIOXIDE USED IN TWELVE HOURS USED IN SUCCESSIVE TWO HOUR INTERVALS

Sample Number	Period					
	0-2	2-4	4-6	6-8	8-10	10-12
Pure iron	34.9	11.1	19.8	9.9	11.1	12.3
C 489	33.0	15.2	24.3	15.2	6.1	6.1
03	23.1	13.9	15.6	15.6	15.6	15.6
01	27.0	8.2	10.8	13.6	19.0	21.7
0 19	34.0	15.1	13.2	18.9	11.3	7.6
C 029	28.0	8.0	24.0	8.0	20.0	12.0
246	25.0	20.3	9.1	20.3	6.8	18.2
25369	33.5	10.3	7.7	10.3	18.0	20.3

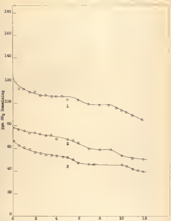

Figure 14.-- Consumption of Sulfur Dioxide by Sample 28369

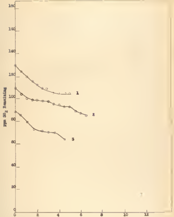

Figure 15.-- Consumption of Sulfur Dioxide by Sample S 489

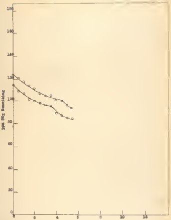

Figure 16.-- Consumption of Sulfur Dioxide by Sample C5

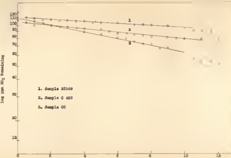

Figure 17.-- Logarithmic Plot of Consumption of Sulfur Dioxide by Several Steels

SUMMARY

An effort has been made to contribute to the knowledge of the corrosion problem by the study of the process occurring when sulfur dioxide attacks iron and ferrous alloys in aqueous solution. The initial phases of this corrosion problem have been investigated polarographically in order to study the possible mechanisms , the order of reaction, and the type of attack.

It has been found that the attack occurs in a step-wise manner consisting of periods of activity on the part of the sulfur dioxide, followed by periods of diminished action. The process is apparently cyclic and shows alternate periods of activity and inhibition throughout the first twelve hour period, this continuing into the next twelve hour interval.

The attack is of first order with respect to the sulfur dioxide. This has been shown through the use of the customary logarithm of the component versus time method developed in the literature.

The mechanism proposed to account for the corrosion is simple, but is in accordance with all information obtained in the investigation. It is supposed that a direct attack upon the iron by the sulfur dioxide occurs. This results in the oxidation of the iron to the ferrous state and the reduction of the sulfur dioxide to the sulfide. A gradually increasing layer of ferrous sulfide forms upon the surface of the metal, eventually preventing further attack. The ferrous sulfide is slowly soluble in the acid media and is dissolved over a period of time to such an extent that the ferrous sulfide coating again becomes permeable and further attack upon the metal can take place. This attack leads to the re-establishment of the ferrous sulfide coating and a new cycle is begun.

No evidence for the presence of any form of sulfur other than the sulfide ion and the sulfur dioxide was obtained in this investigation.

It is quite possible that, as has been suggested,[39] polysulfides as well as sulfide may be formed by the reduction of sulfur dioxide. No evidence was obtained from this work to indicate the absence or presence of polysulfides.

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BIOGRAPHICAL NOTE

Francis John Bowen was born at Humboldt, Iowa, January 17, 1917. He was awarded the degree of Bachelor of Arts by Augustana College, Sioux Falls, South Dakota, in 1938. He then taught at Iroquois High School, Iroquois, South Dakota, until 1939,when he accepted a position as Teaching Fellow in Chemistry at the State College of Washington. He served in this capacity until 1942 when he was awarded the degree of Master of Science. In 1942 he was employed by the Washington State Planning Council to act as research chemist at the Mining Experiment Station, Pullman, Washington. He entered the United States Naval Reserve in 1943, and served until 1946 when he was released to inactive duty with the rank of Lieutenant. Following service in the Navy, Mr. Bowen entered the University of Minnesota as a graduate student and remained at that institution until 1947 when he came to the University of Florida as Interim Instructor.

Mr. Bowen is a member of the American Chemical Society, Alpha Chi Sigma fraternity and the Volunteer Research Reserve of the United States Navy.

COMMITTEE REPORT

This dissertation was prepared under the direction of the Co-Chairman of the Candidate's Supervisory Committee and has been approved by all members of the Committee. It was submitted to the Graduate Council and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

Date. September 2, 1950

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